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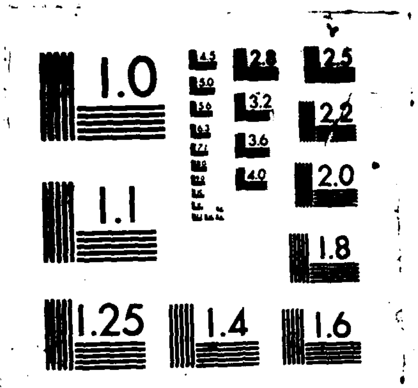

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Synthesis and Characterization of Liquid Crystalline Polyacrylates and Polymethacrylates Containing Benzyl Ether and Diphenyl Ethane Based Mesogens

By

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ABSTRACT

The synthesis and radical polymerization of a novel series of acrylates and methacrylates containing p-cyanophenyl-p-hydroxybenzyl ether, p-methoxyphenyl - p-hydroxybenzyl ether, and 1-(p-cyanophenyl)-2-(p-hydroxyphenyl) ethane groups attached to the polymerizable group through aliphatic spacers containing eleven and six methylenic units is described. The resulting polymers were characterized by differential scanning calorimetry and optical polarization microscopy. All polymers exhibited enantiotropic mesomorphism. Low molar mass compounds based on benzyl ether or diphenyl ethane units exhibit only monotropic or virtual transitions. This demonstrates that the "polymer effect" stabilizes mesophases obtained from "mesogenic units" which do not contain rigid interconnecting groups.

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Synopsis

The synthesis and radical polymerization of a novel series of acrylates and methacrylates containing p-cyanophenyl-p-hydroxybenzyl ether, p-methoxyphenyl - p-hydroxybenzyl ether, and 1-(p-cyanophenyl)-2-(p-hydroxyphenyl) ethane groups attached to the polymerizable group through aliphatic spacers containing eleven and six methylenic units is described. The resulting polymers were characterized by differential scanning calorimetry and optical polarization microscopy. All polymers exhibited enantiotropic mesomorphism. Low molar mass compounds based on benzyl ether or diphenyl ethane units exhibit only monotropic or virtual transitions. This demonstrates that the "polymer effect" stabilizes mesophases obtained from "mesogenic units" which do not contain rigid interconnecting groups.

INTRODUCTION

In the last years, the relationship between the chemical structure and the properties of low molecular mass liquid crystals underwent such a development that organic chemists could safely state: "contrary to the theoretician's belief, the constituent molecules of liquid crystals are neither rigid nor cylindrically symmetric" (1). This relationship has been extensively discussed and reviewed (1-10).

Recently, we became interested in the synthesis of liquid crystal polymers containing mesogenic units which undergo conformational isomerism. The first examples described by us refer to liquid crystalline polymers containing trans-2,5-disubstituted-1,3-dioxanes (11-14) and 2,5-disubstituted-1,3,2-dioxaborinane (15) based mesogens. The second examples refer to mesogenic units in which the interconnecting group between two aromatic or cycloaliphatic units represents a flexible "ethyl" or "methyleneoxy" linkage. Although ethane and methyleneoxy units, can adopt a similar conformation with a rigid ester group, they are flexible, and therefore, undergo free rotation leading to a number of different conformational isomers. Of these conformational isomers, the one providing an extended structure, i.e., "anti" or "antiperiplanar" would certainly have to exhibit similar properties when compared to the structure constructed with an ester interconnecting unit. The conformational isomers are in dynamic equilibrium, and at the present time there is no information in the literature concerning the influence of a mesomorphic phase on the conformational equilibrium, or of the conformational equilibrium on the mesomorphic behavior.

In a previous paper (16), we have presented the synthesis and characterization of side-chain liquid crystalline polysiloxanes containing benzyl ether based mesogens.

The goal of this paper is to present the synthesis and characterization of a series of liquid crystalline polyacrylates and polymethacrylates containing benzyl ether and diphenyl ethane based mesogens, and to compare their mesomorphic behaviors.

EXPERIMENTAL

A. Materials

p-Bromophenyl acetic acid (Lancaster Synthesis), 11-bromo-1-undecanol, 0.5 M solution of 9-borabicyclo-[3.3.1]nonane (9-BBN) in tetrahydrofuran, 1M BBr_3 in CH_2Cl_2 (Aldrich), methacryloyl chloride, and acryloyl chloride (Fluka) were used as received. Anisole (Aldrich) was distilled from calcium hydride. 1,4-Dioxane was first refluxed over sodium and then distilled under argon. α,α'-Azoisobutyronitrile (AIBN) (Fluka) was freshly recrystallized from methanol (below 40°C). All the other reagents were used as received.

B. Techniques

200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ solution with TMS as internal standard. A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions which were read at the maximum of their endothermic or exothermic peaks. In all cases, heating and cooling rates were 20°C/min unless otherwise specified. Glass transition temperatures (Tg) were read at the middle of the change in the heat capacity. After the first heating scan, the sample was "annealed" at about 10°C above the

isotropization temperature for 5-10 min. Under these registration conditions, beginning with the second heating and cooling scans all the DSC scans gave perfectly reproducible data. The transitions reported were read during the second or third heating and cooling scans unless otherwise specified. A Carl-Zeiss optical polarizing microscope (magnification: 100x) equipped with a Mettler FP80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.

GPC and HPLC analyses were carried out with a Perkin-Elmer series 10LC instrument equipped with LC-100 column oven, LC-600 autosampler, and Sigma 15 data station. The molecular weights are relative to polystyrene standards. The measurements were made by using an UV detector, THF as solvent (1 ml/min, 40°C), a set of PL-gel columns of 10^2, 5×10^2, 10^3, 10^4 and 10^5 Å, and a calibration plot constructed with polystyrene standards.

C. Syntheses of Monomers and Polymers

The syntheses of monomers are outlined in Scheme 1 and Scheme 2.

p-Cyanophenyl-p-(1-undecenyl-11-oxy) benzyl ether and p-methoxyphenyl-p-(1-undecenyl-11-oxy) benzyl ether

Both benzyl ethers were synthesized as reported in a previous publication from our laboratory (16).

p-Cyanophenyl-p-(1-hydroxyundecanyl-11-oxy) benzyl ether and p-methoxyphenyl-p-(1-hydroxyundecanyl-11-oxy) benzyl ether

Both benzyl ethers were synthesized by the hydroboration of the corresponding alkene. An example is described below. In a dry three-neck

flask equipped with a thermometer, a pressure-equilibrated dropping funnel, and a reflux condenser fitted with an N_2 adapter and connected to a silicon oil bubbler was placed a solution of p-cyanophenyl-p-(1-undecenyl-11-oxy) benzyl ether (3.1 g, 6.85 mmole) in dry THF (5 ml). 9-BBN (13.7ml, 6.85 mmole) 0.5 M solution in THF was charged via a syringe into the dropping funnel, and then added slowly into the stirring olefin solution. After the addition was completed, the mixture was oxidized. A solution of 3N NaOH (3ml) was injected into the flask followed by 5 ml of 30% H_2O_2 solution, which were added dropwise over 15 min. The reaction mixture was stirred for one additional hr and poured into water. The precipitated product was filtered, washed with water, dried, and recrystallized from toluene. Yield: 2.8 g (87%). m.p. = 92-93°C. The ^{1}H-NMR spectra of both compounds are reported in Table I.

p-Bromobenzyl p-methoxyphenyl ketone

4-Bromophenyl acetic acid (21.5g, 0.1 mole) was dissolved in 200 ml of dry dichloromethane and 8.9 ml (0.12 mole) of thionyl chloride were added dropwise. After the addition was completed, the solution was stirred at room temperature for 3 hours. The solvent and the excess of thionyl chloride were removed by distillation and the remaining solid was dried in a vacuum oven overnight. The acid chloride was dissolved in 50 ml of dry dichloromethane and added slowly to a cooled mixture of 10 g (0.093 mole) anisole and 26.6 g (0.2 mole) anhydrous aluminum trichloride in 100 ml of dichloromethane. The reaction mixture was stirred at room temperature for 3 hrs and then poured into a mixture containing 50 g ice, 50 ml water, and 50 ml concentrated hydrochloric acid. The organic layer was isolated, washed with 2% $NaHCO_3$ aqueous solution, water, and

dried over anhydrous $MgSO_4$. The solid obtained after the solvent was evaporated was recrystallized from ethanol to yield 12.5 g (44%). m.p. = 138°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 3.87 (s, 3H, $-OC\underline{H}_3$), 4.18 (s, 2H, $Ph-C\underline{H}_2CO-$) 6.90-7.98 (m, 8 aromatic protons).

<u>1-(p-Bromophenyl)-2-(p-methoxyphenyl) ethane</u>

To a solution of $LiAlH_4$ (3.42 g, 0.09 mole) in dry diethyl ether (50 ml) was added dropwise a solution of anhydrous $AlCl_3$ (11.97 g, 0.09 mole) in dry diethyl ether (50 ml). The mixture was cooled to -40°C (dry ice-methanol) and a solution of p-bromobenzyl p-methoxyphenyl ketone (12.2 g, 0.04 mole) in chloroform (150 ml) was added slowly. After the addition was completed the reaction mixture was stirred at room temperature for 3 hrs. and then a mixture containing 100 ml of conc. hydrochloric acid and 125 ml of water was carefully added to the reaction mixture. The organic layer was separated, washed with 2% $NaHCO_3$ aqueous solution, water, and dried over anhydrous $MgSO_4$. The solvent was removed on a rotavapor, and the remaining solid was recrystallized from methanol to yield 9.6 g, (82%). m.p. = 79-80°C. ^{1}H-NMR ($CDCl_3$ TMS, δ , ppm): 2.83 (s, 4H, $-Ph-C\underline{H}_2C\underline{H}_2-Ph-$), 3.78 (s, 3H, $Ph-OC\underline{H}_3$), 6.76-7.36 (m, 8 aromatic protons).

<u>1-(p-Bromophenyl)-2-(p-hydroxyphenyl) ethane</u>

a) <u>By demethylation with HBr/CH_3COOH</u>

1-(p-Bromophenyl)-2-(p-methoxyphenyl)ethane (9.5g, 0.0326 mole) was dissolved in a mixture containing acetic acid (200 ml) and 48% hydrobromic acid (200 ml) and then heated under reflux for 30 min. The solution was evaporated in vacuo, and diethyl ether (200 ml) was added to the residue. The ethereal

solution was washed with dilute aqueous solution of $NaHCO_3$, and then water. The crude product obtained on evaporation of solvent was dissolved in hot dilute NaOH solution and reprecipitated by acidification (dilute hydrochloric acid). The precipitate was filtered, dried, and recrystallized from a mixture of 1/1 (V/V) ethanol-water to yield 5 g (55%). m.p. = 123-124°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.83 (s, 4H, -Ph-$C\underline{H}_2C\underline{H}_2$-Ph-), 6.71 to 7.38 (m, 8 aromatic protons).

b) <u>By demethylation with BBr_3</u>

A solution of 1-(p-bromophenyl)-2-(p-methoxyphenyl) ethane (12 g, 0.041 mole) in dry methylene chloride (120 ml) was cooled to -78°C (dry-ice-acetone) and 45 ml of 1M BBr_3 in dry methylene chloride were added dropwise under nitrogen. The reaction mixture was allowed to warm up to room temperature and stirred overnight. Water (75ml) was then added, and the solution was extracted with diethyl ether. The ethereal solution was washed with water, dried over anhydrous Na_2SO_4, and then evaporated to dryness. The obtained product was recrystallized from a mixture of 1/1 (V/V) ethanol-water to yield 9.4 g (82.6%). m.p. = 123-124°C.

<u>1-(p-Cyanophenyl)-2-(p-hydroxyphenyl) ethane</u>

Copper (I) cyanide (1.95 g, 0.0217 mole) was added to a solution containing 1-(p-bromophenyl)-2-(p-hydroxyphenyl) ethane (4.0 g, 0.0145 mole) in dry N-methylpyrrolidinone (50 ml). The reaction mixture was refluxed for 1.5 hrs., cooled to 100°C and poured into a solution of iron (III) chloride (4.2 g) in water (6.5 ml) and concentrated hydrochloric acid (2.3 ml), and then stirred at 60°C for 30 min. The obtained mixture was extracted with diethyl ether. The ethereal solution was treated with charcoal, dried over anhydrous sodium

sulfate, and then evaporated to dryness. The solid was purified by column chromatography (silica gel, chloroform as eluent) to yield 2.25 g (70%). m.p. = 149-150°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 2.90 (m, 4H), -Ph-$C\underline{H}_2C\underline{H}_2$-Ph-), 6.71-7.54 (m, 8 aromatic protons).

<u>1-(p-Cyanophenyl)-2-(p-(1-hydroxyundecanyl-11-oxy)phenyl) ethane (III) and 1-(p-cyanophenyl)-2-(p-(1-hydroxyhexanyl-6-oxy) phenyl) ethane (IV)</u>

Both III and IV were synthesized by the same method. An example is described below. Freshly cut Na (0.23g, 0.01 mole) was added in portions to 50 ml of absolute ethanol. After the sodium was completely dissolved, 2.23 g (0.01 mole) of 1-(p-cyanophenyl)-2-(p-hydroxyphenyl) ethane were added. The alcohol was removed on a rotavapor to isolate the sodium salt of the substituted phenol. The dried sodium salt was dissolved in dry N-methyl-2-pyrrolidinone (60 ml) and 11-bromoundecan-1-ol (2.51 g, 0.01 mole) was added. The reaction mixture was stirred at 110°C under N_2 overnight, and then poured into water. The precipitated product was filtered, washed with dilute aqueous NaOH solution, water, dried and recrystallized from n-hexane to yield 3.3 g (84%). m.p. = 69-70°C. The ^{1}H-NMR spectra of both compounds are reported in Table I.

<u>Synthesis of I-MA, I-AC, II-MA, II-AC, III-MA, III-AC, IV-MA and IV-AC</u>

All methacrylates and acrylates were synthesized by the esterification of the corresponding alcohol (I, II, III and IV from Schemes 1 and 2) with methacryloyl chloride or acryloyl chloride. An example of their synthesis is as follows: p-cyanophenyl-p-(1-hydroxyundecanyl-11-oxy) benzyl ether (1.0 g, 2.13 mmole) was dissolved in a mixture of dried THF (30 ml) and triethylamine (0.5 ml, 3.3 mmole). The resulting solution was cooled in an ice-water bath to 0°C,

and methacryloyl chloride (0.25 ml, 3.19 mmole) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature, and then stirred overnight. After the solution was poured into water, the precipitated product was filtered, dried under vacuum, and purified by column chromatography (silica gel, chloroform as eluent) to yield 0.95 g (83%). Table I presents the ^{1}H-NMR spectra of the synthesized monomers, while Table II summarizes their thermal behavior.

D. Polymerizations

The radical polymerizations of the monomers were carried out in Schlenk tubes equipped with septa , under argon. The polymerization tube containing the dioxane solution of the monomer (10%, wt/vol) and the initiator (AIBN, 1 wt% vs monomer) was first degassed by several freeze - pump - thaw cycles under vacuum, and then filled with argon. All polymerizations were carried out at 60°C for 15 hrs. After the polymerization time, the polymers were precipitated into methanol, filtered, and purified by reprecipitation from THF solutions into methanol. Table III summarizes the polymerization results.

RESULTS AND DISCUSSION

The idea of replacing interconnecting ester groups of mesogenic units with methyleneoxy (17-29) or ethane (17, 23, 25-28, 30-36) groups has been pursued by organic chemists working in the field of low molar mass liquid crystals only recently. Both methyleneoxy and ethane groups were successful in stabilizing the mesophase, particularly when they were used to interconnect two cycloaliphatic units, or an aromatic and a cycloaliphatic unit. Low molar mass

liquid crystals containing a methyleneoxy unit in between two aromatic groups were reported only recently (24,29). Although most of the low molar mass liquid crystals based on benzyl ethers present only monotropic or virtual transitions (16,24,29), their polymeric homologues exhibit enantiotropic mesomorphism (16). This represents an excellent example of mesophase stabilization by the polymer backbone (37,38).

The synthesis of methacrylates and acrylates containing benzyl ether based mesogens is described in Scheme 1. p-(1-Undecylenyl-11-oxy) benzyl ethers of 4-cyanophenol and 4-methoxyphenol were synthesized by a method previously developed in our laboratory (16). The hydroboration of the olefinic groups with 9-BBN (39,40) gave only primary alcohols, which by esterification with methacryloyl or acryloyl chlorides led to the corresponding monomers.

The synthetic routes used for the preparation of methacrylates and acrylates containing 1-(p-cyanophenyl-2-(p-hydroxyphenyl) ethane based mesogens are outlined in Scheme 2. There are only few details we want to mention. We preferred to reduce the keto group directly to the $-CH_2-$ group by using the $LiAlH_4/AlCl_3$ reagent (41,42) rather than the Wolff-Kishner reaction. The first method was always quantitative, although performed under mild reaction conditions. We also recommend the demethylation of the methoxy group with BBr_3 in CH_2Cl_2 (43), rather than with HBr in CH_3COOH. Both the yield, and the purity of the demethylated product obtained by using BBr_3 were higher than that of the same product obtained by using HBr.

The thermal characterization of the monomers was performed both by DSC and optical polarization microscopy. Since all the monomers undergo thermal polymerization, their characterization is difficult. Table II summarizes their

thermal transitions obtained from DSC measurements. Apparently only the monomers II-MA and III-AC present a smectic monotropic liquid crystalline mesophase.

Table III summarizes the results of the radical polymerization of the monomers. Since their molecular weights were determined by GPC by using a calibration based on polystyrene standards, they have only a qualitative meaning. In addition, it is well known that side-chain liquid crystalline polymers form aggregates in solution (44), and this also affects their molecular weight determinations.

The results of the thermal characterization of the polymers are presented in Table IV. All polymers exhibited enantiotropic mesomorphism. Several conclusions can be obtained from this table. Although the molecular weights of the polyacrylates are lower than of the corresponding polymethacrylates (Table III), the isotropization temperatures for all polyacrylates are higher than of the corresponding polymethacrylates. This suggests that a flexible backbone stabilizes the mesophase more than a rigid backbone does. Poly (IV-MA) is the only polymer which exhibits a nematic mesophase. This result confirms previous conclusions concerning the influence of the length of the spacer on the type of mesophase formed (45,46) i.e., long spacers favor a smectic mesophase while short spacers favor a nematic one. The corresponding poly (IV-AC) is smectic, suggesting again that a more flexible backbone tends to give a more organized mesophase.

By comparing the phase transitions of the polymers poly (III-MA), poly (III-AC) (both containing eleven methylenic units in the spacer) with those of the poly (IV-MA) and poly (IV-AC) (both containing six methylenic units in the

spacer) we can conclude that a short spacer gives a lower isotropization temperature than a long spacer does.

The polymers poly (I-MA) and poly (I-AC) have the same spacer length (eleven methylene units) as the polymers poly (III-MA) and poly (III-AC) and the same substituent in the 4 position of the mesogen (a cyano group). The only difference is due to the interconnecting group present in the middle of the mesogenic unit, i.e., the former polymers contain a benzyl ether unit while the latter polymers contain an ethane unit. Although the polymethacrylates have different molecular weights, their isotropization temperature is the same, i.e., 68°C. The polyacrylate with an ethane interconnecting unit has a lower isotropization temperature than the polymer with a benzyl ether unit. In all cases the polymers containing ethane interconnecting units exhibit one more liquid crystalline mesophase than the polymers with benzyl ether units.

Although all polymers exhibit typical textures for different classic mesophases, optical polymerization microscopy coupled with DSC are not sufficient to definitively assign their mesophases. A representative example of focal-conic fan shape texture observed for the liquid crystalline polymer poly (II-MA) is presented in Figure 2. It represents the smectic mesophase from the high range of temperature of the DSC thermogram presented in Figure 2. The first mesophase after the glass transition temperature is not mobile enough to give a representative texture, even after long annealing.

In conclusion, although low molar mass compounds containing either methyleneoxy or ethane groups as interconnecting units in between two phenyl rings do not give rise to thermally stable mesophases, their attachement as side groups to polymeric systems lead to enantiotropic liquid crystalline polymers.

Both types of mesogenic units can be prepared in high yields by using simple preparative methods and at the same time are hydrolytically stable; therefore, this novel class of polymers provides an interesting alternative to the synthesis of side-chain liquid crystalline polymers containing ester groups in their mesogenic units.

Acknowledgements

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Figure and Scheme Captions

Figure 1: Optical polarization micrograph (100x) presenting the smectic focal-conic fan texture of the poly (II-MA): 70^{o}C, cooling scan.

Figure 2: Normalized DSC thermograms heating and cooling rates: 20^{o}C/min of the poly (II-MA): A) Second heating scan; B) Second cooling scan.

Scheme 1: Synthesis of methacrylates and acrylates containing benzyl ether based mesogens.

Scheme 2. Synthesis of methacrylates and acrylates containing 1-(p-cyanophenyl)-2-(p-hydroxyphenyl) ethane based mesogens.

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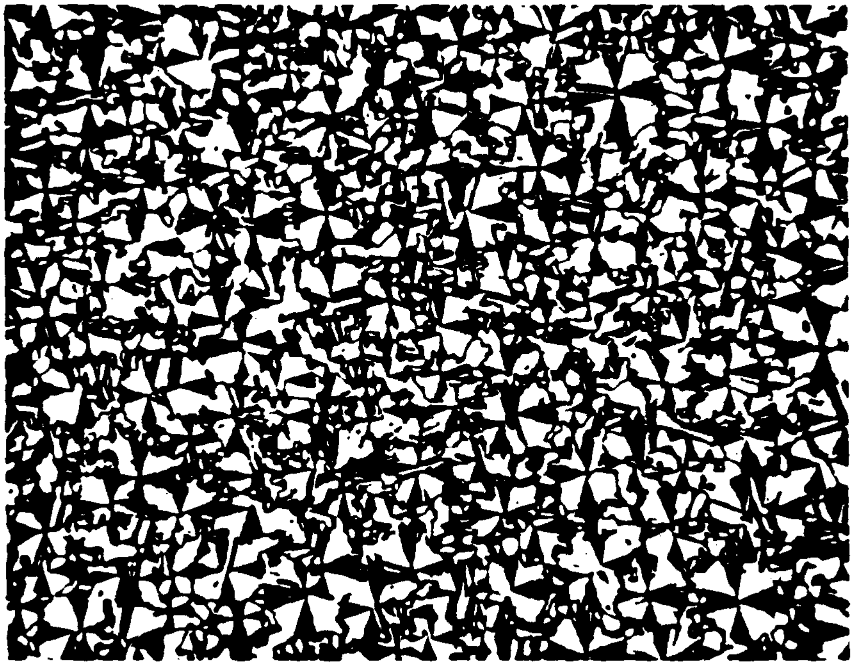


Figure 1

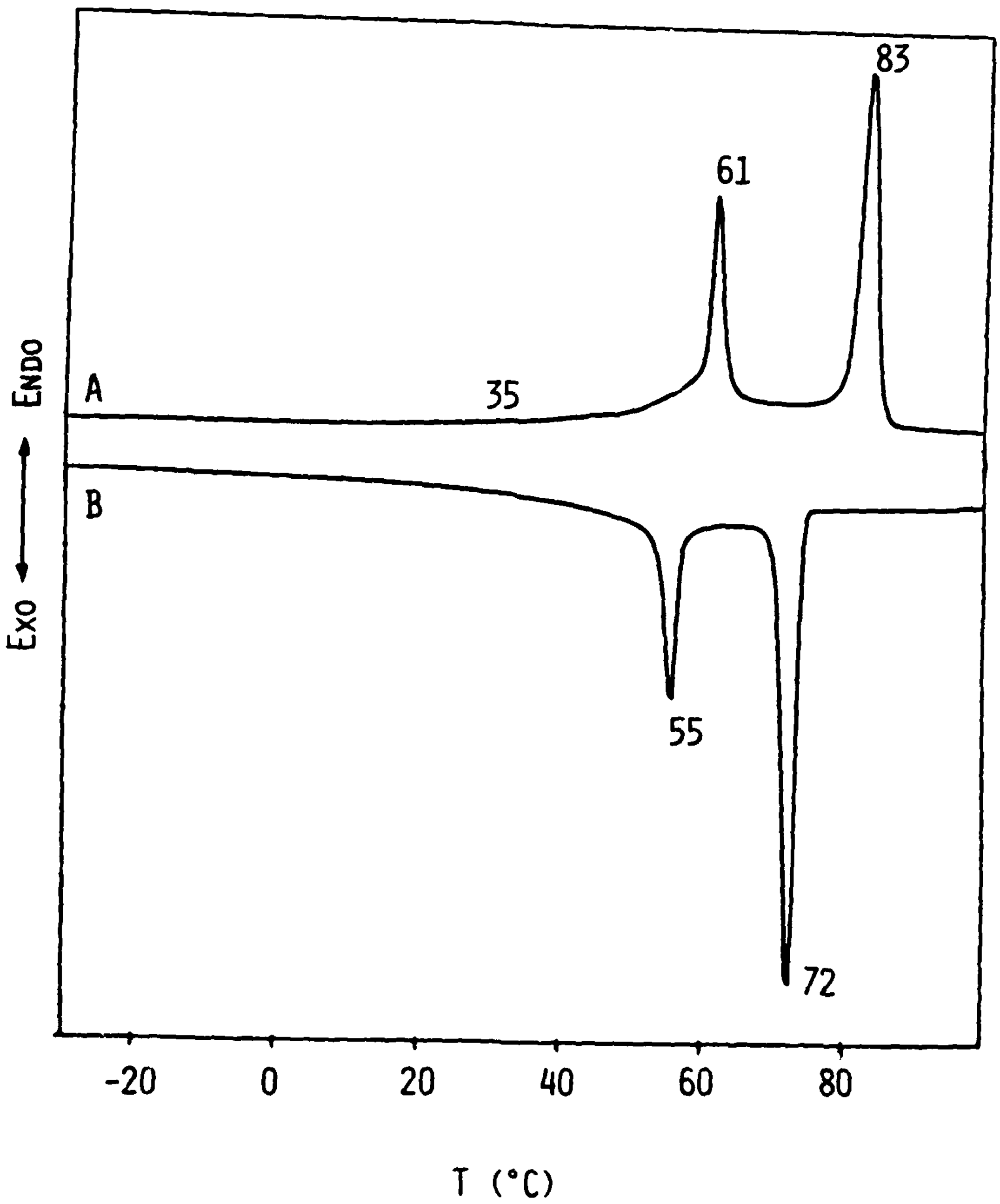
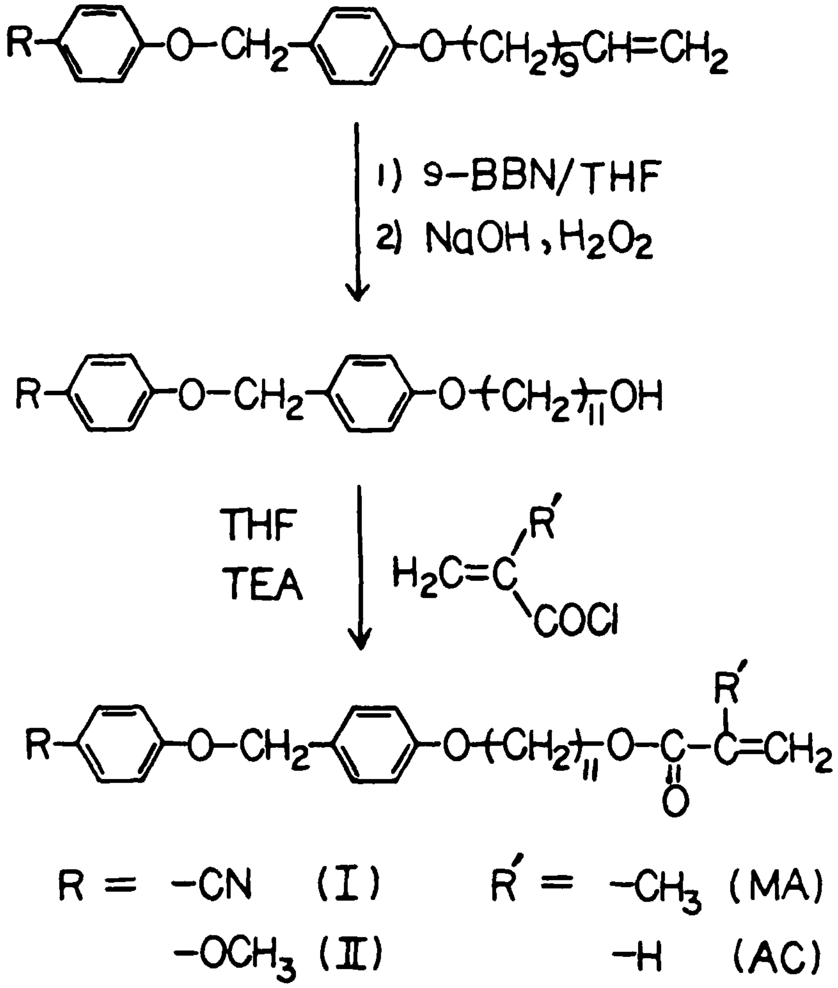
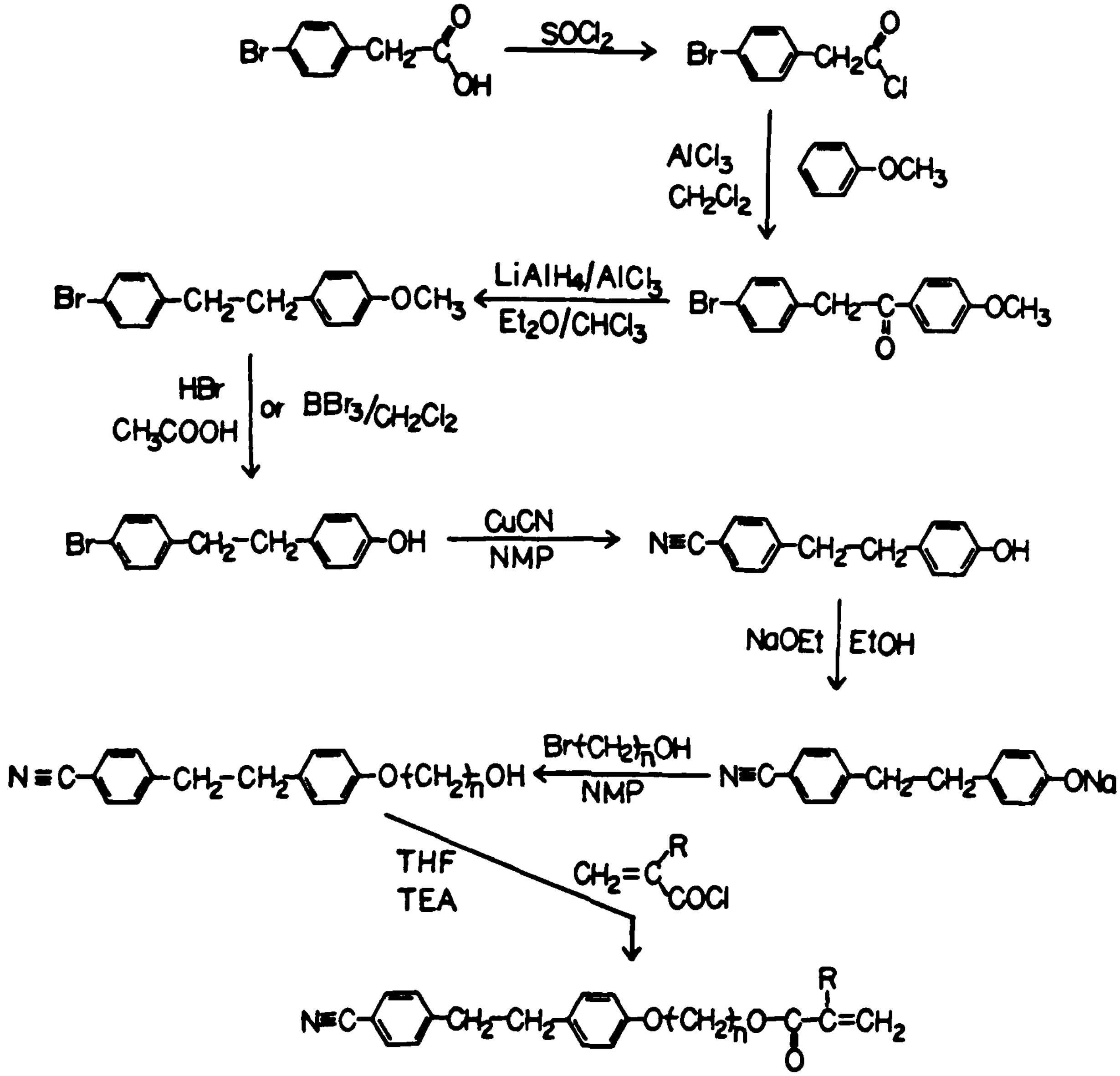


Figure 2



Scheme 1

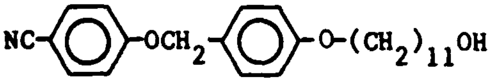
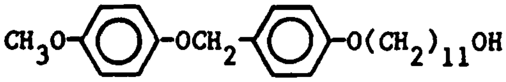
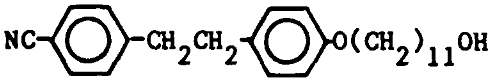
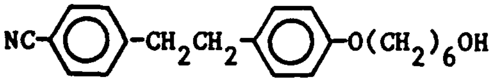
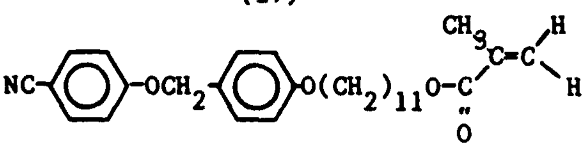
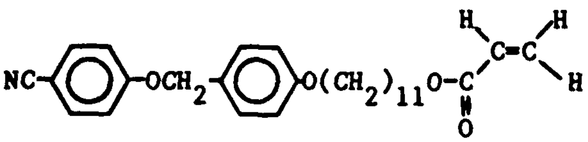


	n=11 , 6
R = $-CH_3$	(III , IV–MA)
$-H$	(III , IV–AC)

Scheme 2

<u>Table I</u>

Characterization of Monomers and Intermediary Compounds

Compound	200 MHz ^{1}H-NMR (δ, ppm)
 (I)	1.31 to 1.81 (m,$-(C\underline{H})_9-$); 3.63 (t, $-C\underline{H}_2OH$); 3.96 (t, Ph-$OC\underline{H}_2-$); 5.02 (s, Ph-$C\underline{H}_2O$-Ph); 6.86 to 7.58 (4d, 8 aromatic protons).
 (II)	1.33 to 1.81 (m, $-(C\underline{H}_2)_9-$); 3.63 (t, $-C\underline{H}_2OH$); 3.77 (s, $-OC\underline{H}_3$); 3.96 (t, Ph-$OC\underline{H}_2-$); 4.97 (s, Ph-$C\underline{H}_2O$-Ph); 6.83 to 7.33 (m, 8 aromatic protons).
 (III)	1.30 to 1.80 (m, $-(C\underline{H}_2)_9-$); 2.91(m, Ph-$C\underline{H}_2C\underline{H}_2$-Ph); 3.63 (t, $-C\underline{H}_2OH$); 3.96 (t, Ph-$OC\underline{H}_2-$); 6.77 to 7.54 (4d, 8 aromatic protons).
 (IV)	1.37 to 1.85 (m, $-(C\underline{H}_2)_4-$); 2.90 (m, Ph-$C\underline{H}_2C\underline{H}_2$-Ph); 3.66 (t, $-C\underline{H}_2OH$); 3.94 (t, Ph-$OC\underline{H}_2-$); 6.77 to 7.54 (4d, 8 aromatic protons).
 (I-MA)	1.31 to 1.81 (m, $-C\underline{H}_2)_9-$); 1.96 (s. $C\underline{H}_3-C{=}C$); 3.96 (t, Ph-$OC\underline{H}_2-$); 4.13 (t, $-C\underline{H}_2O\overset{\|}{C}-$); 5.02 (s, Ph-$C\underline{H}_2O$-Ph); 5.54 and 6.10 (m, $-\overset{\vert}{C} = C\underline{H}_2$); 6.88 to 7.58 (4d, 8 aromatic protons).
 (I-AC)	1.31 to 1.81 (m, $-(C\underline{H}_2)_9-$); 3.96 (t, Ph-$OC\underline{H}_2-$); 4.15 (t, $-C\underline{H}_2O\overset{\|}{C}-$), 5.03 (s, Ph-$C\underline{H}_2O$-Ph); 5.78 to 6.44 (m, $-C\underline{H} = C\underline{H}_2$); 6.88 to 7.60 (4d, 8 aromatic protons).

continued...

Table I, continued

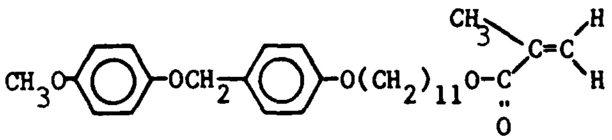
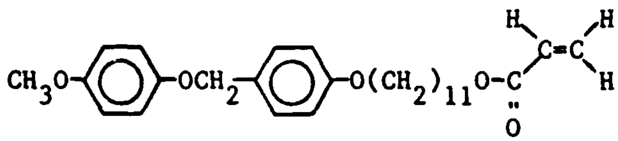
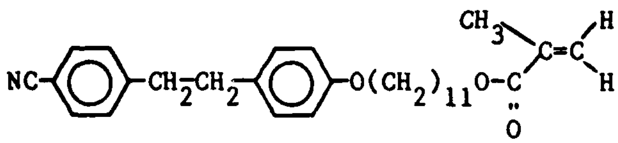
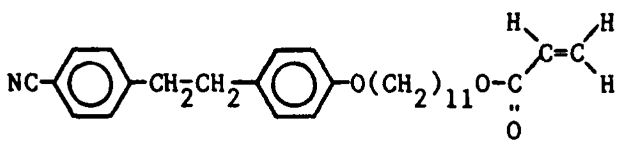
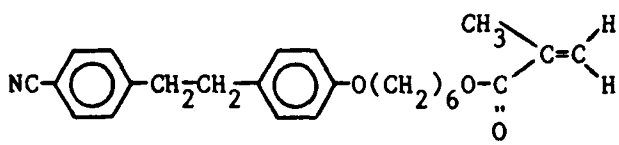
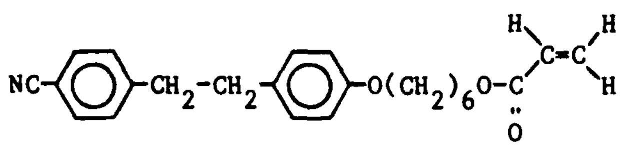
Compound	200 MHz ^{1}H-NMR (δ, ppm)
 (II-MA)	1.30-1.81 (m, $-(CH_2)_9-$); 1.96 (s, $C\underline{H}_3-C{=}C$); 3.77 (s, $-OC\underline{H}_3$); 3.96 (t, Ph-$OC\underline{H}_2-$); 4.13 (t, $-C\underline{H}_2-O\overset{\|}{C}-$); 4.93 (s, Ph-$OC\underline{H}_2$-Ph); 5.53 and 6.08 (m, $-\overset{\mid}{C}{=}C\underline{H}_2$); 6.83 to 7.33 (m, 8 aromatic protons).
 (II-AC)	1.30-1.81 (m, $-(CH_2)_9-$); 3.77 (s, $-OC\underline{H}_3$); 3.96 (t, Ph-$OC\underline{H}_2-$); 4.13 (t, $-C\underline{H}_2O\overset{\|}{C}-$); 4.93 (s, Ph-$OC\underline{H}_2-$ Ph); 5.76 to 6.43 (m, $-C\underline{H}{=}C\underline{H}_2$); 6.83 to 7.33 (m, 8 aromatic protons).
 (III-MA)	1.30 to 1.80 (m, $-(C\underline{H}_2)_9-$); 1.96 (s, $C\underline{H}_3-C{=}C$); 2.90 (m,Ph-$C\underline{H}_2C\underline{H}_2$-Ph);3.93 (t, Ph-$OC\underline{H}_2-$); 4.16 (t, $-C\underline{H}_2O\overset{\|}{C}-$); 5.54 and 6.08 (m, $-\overset{\mid}{C}{=}C\underline{H}_2$); 6.77 to 7.54 (4d, 8 aromatic protons).
 (III-AC)	1.30 to 1.80 (m, $-(C\underline{H}_2)_9-$); 2.90 (m, Ph-$C\underline{H}_2C\underline{H}_2$-Ph); 3.93 (t, Ph-$OC\underline{H}_2-$); 4.16 (t, $-C\underline{H}_2O\overset{\|}{C}-$); 5.78 to 6.44 (m, $-C\underline{H}{=}C\underline{H}_2$); 6.77 to 7.54 (4d, 8 aromatic protons).
 (IV-MA)	1.37 to 1.81 (m,$-(C\underline{H}_2)_4-$); 1.96 (s, $C\underline{H}_3-C{=}C$); 2.90 (m, Ph-$C\underline{H}_2C\underline{H}_2$-Ph); 3.93 (t, Ph-$OC\underline{H}_2-$); 4.17 (t, $-C\underline{H}_2O\overset{\|}{C}-$); 5.54 and 6.08 (m, $-\overset{\mid}{C}{=}C\underline{H}_2$); 6.76 to 7.54 (4d, 8 aromatic protons).
 (IV-AC)	1.38 to 1.81 (m, $-(CH_2)_4-$); 2.90 (m, Ph-$C\underline{H}_2C\underline{H}_2$-Ph); 3.93 (t, Ph-O-$C\underline{H}_2-$); 4.17 (t, $-C\underline{H}_2O-\overset{\|}{C}-$); 5.78 to 6.44 (m, $-C\underline{H}{=}C\underline{H}_2$); 6.76 to 7.54 (4d; 8 aromatic protons).

Table II

Thermal Transitions and Thermodynamic Parameters of Monomers

Monomer Type	Thermal Transitions (°C) and Thermodynamic Parameters: ΔH(kcal/mole); ΔS(cal/mole.°K)						
	Heating			Cooling			
	Tm	ΔHm	ΔSm	Ti	Tc	ΔHc	ΔSc
I-MA	82	11.5	32.4	--	59	9.4	28.4
I-AC	99	16.0	43.0	--	57	13.7	41.5
II-MA	73	13.9	40.1	55	53	13.2[a)]	--
II-AC	69	14.7	42.9	--	53	9.1	27.8
III-MA	57	11.2	33.8	--	27	9.2	30.8
III-AC	82	13.6	38.4	61	64.5	11.4[a)]	--
IV-MA	37	8.6	27.7	--	--	--	--
IV-AC	74	8.4	24.2	--	--	--	--

a) $\Delta H_C = \Delta Hc + \Delta Hi$

Table III

Radical Polymerization of Monomers

Monomer Type	Conversion %	$\overline{M}n \times 10^{-3}$	$\overline{M}w \times 10^{-3}$	$\overline{M}w/\overline{M}n$
I-MA	82	7.1	10.2	1.42
I-AC	77	6.0	8.0	1.32
II-MA	76	26.4	39.3	1.49
II-AC	82	7.14	10.3	1.44
III-MA	81	30.3	45.5	1.50
III-AC	78	9.36	13.4	1.43
IV-MA	80	19.0	30.2	1.58
IV-AC	76	9.16	14.8	1.62

Table IV

Thermal Transitions and Thermodynamic Parameters of Polymers

Polymer	Thermal Transitions (^{o}C) and Thermodynamic Parameters: ΔH(Kcal/mru)*; ΔS(cal/mru ^{o}K)*																
	Heating									Cooling							
Type	Tg	Tm	ΔHm/ΔSm	Tl	ΔHl/ΔSl	T2	ΔH2/ΔS2	Ti	ΔHi/ΔSi	Ti	ΔHi/ΔSi	T2	ΔH2/ΔS2	Tl	ΔHl/ΔSl	Tc	ΔHc/ΔSc
Poly(I-MA)	19	64	—	—	—	—	—	68	1.94[a]/—	53	1.61[a]/—	—	—	—	—	34	—
Poly(I-AC)	19	72	—	77	2.37[b]/—	—	—	84	0.15/0.41	66	1.10[c]/—	—	—	60	—	45	1.02/3.22
Poly(II-MA)	35	—	—	61	1.31/3.92	—	—	83	2.13/5.98	72	2.13/6.18	—	—	55	0.95/2.91	—	—
Poly(II-AC)	36	63	0.49/1.46	85	—	—	—	92	4.97[c]/—	72	4.86[d]/—	65	—	57	—	—	—
Poly(III-MA)	3	—	—	56	0.63/1.90	—	—	68	1.47/4.32	54	1.48/4.53	—	—	46	0.60/1.89	—	—
Poly(III-AC)	16	—	—	28	—	34	0.98[f]/—	72	1.25/3.61	63	1.22/3.63	26	0.90[f]/—	22	—	—	—
Poly(IV-MA)	29	—	—	—	—	—	—	49	0.23/0.70	41	0.22/0.71	—	—	—	—	—	—
Poly(IV-AC)	20	—	—	—	—	—	—	60	0.70/2.12	55	0.68/2.08	—	—	—	—	—	—

* mru = mole repeat unit

a = Overlapped transition : ΔHi = ΔHi + ΔHm

b = Overlapped transition : ΔHl = ΔHl + ΔHm

c = Overlapped transition : ΔHi = ΔHi + ΔHl

d = Overlapped transtiion : ΔHi = ΔHi + ΔHl + ΔH2

e = Overlapped transition : ΔH2 = ΔH2 + ΔHl

END
9-87
DTIC